How harmonic is dipole resonance of metal clusters?

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Abstract

We discuss the degree of anharmonicity of dipole plasmon resonances in metal clusters. We employ the time-dependent variational principle and show that the relative shift of the second phonon scales as $N^{-4/3}$ in energy, N being the number of particles. This scaling property coincides with that for nuclear giant resonances. Contrary to the previous study based on the boson-expansion method, the deviation from the harmonic limit is found to be almost negligible for Na clusters, the result being consistent with the recent experimental observation.

Collective phonon excitations are common phenomena in fermionic many-body systems. In alkali metal clusters, a very strong dipole plasmon resonances have been observed in the electromagnetic response, which are interpreted as collective vibrational excitations of an electron gas against a background ions [1]. These resonances are well described in the random phase approximation (RPA) as a particle-hole excitaion, which assumes the harmonic nature of the vibrations [2]. It may thus be a natural idea to expect the existence of multiple plasmon excitations. It is worth mentioning that double phonon excitations have been observed in a similar phenomenon in nuclear physics, i.e. giant dipole resonance [3,4].

One interesting question is whether the dipole plasmon resonance in metal clusters is harmonic enough to allow multiple excitations. Catara *et al.* used the boson-expansion method to discuss two-plasmon excitations in metal clusters [5]. They claimed that anharmonic effects are quite large. On the other hand, a comparison between a jellium-RPA calculation and the result of time-dependent local density approximation (TDLDA) [6] suggests that the anharmonic effects are very small for Na clusters. Recently an experiment was performed which addresses the anharmonic properties of plasmon resonances of alkali metal clusters [7]. In this experiment, a large intensity of doubly and triply charged fragments were obserbed in the charge distribution of photofragment of Na_{93}^+. The ionization energy of this cluster lies between the energy of single and double plasmon resonances, and the photon energy was set to be slightly larger than the one plasmon energy. The ionization was thus energetically possible only if at least two photon are absorbed. The observed ionization was interpreted as electron emission via multiple plasmon states, suggesting a very small anharmonicity, which does not support the prediction by Catara *et al.* This picture was later confirmed theoretically, although a significant correction from a direct two photon absorbtion was reported [8].

The aim of this paper is to show that the anharmonic effects are indeed very small for the dipole plasmon resonance in metal clusters, contrary to the prediction by Catara *et al.* To this end, we apply the variational principle for the time-dependent Schrödinger equation. The time-dependent variational principle was recently applied to large amplitude collective

motions to discuss anharmonic properties of nuclear giant resonances [9]. Its applicability has been tested on a solvable model in Ref. [10]. The time-dependent variational approach allows one to estimate relatively easily the energy shift of double phonon state with an analytic formula. As we will see, it has the same scaling law concerning the number of particle for both nuclear and cluster cases, although the range of the interaction is very different for these two systems.

Consider a system where N electrons interact with each other in a positively charged ionic background whose density is given by $\rho_I(\boldsymbol{r})$. The Hamiltonian for this system is given by

$$H = \sum_{i=1}^{N} \frac{\boldsymbol{p}_i^2}{2m} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} + \sum_{i=1}^{N} V_I(\boldsymbol{r}_i), \tag{1}$$

where m is the electron mass. $V_I(\boldsymbol{r})$ describes the interaction between the electrons and the ionic background. It is given by

$$V_I(\boldsymbol{r}) = -e^2 \int d\boldsymbol{r}_I \frac{\rho_I(\boldsymbol{r}_I)}{|\boldsymbol{r} - \boldsymbol{r}_I|}, \tag{2}$$

and satisfies the Poisson equation

$$\nabla^2 V_I(\boldsymbol{r}) = 4\pi e^2 \rho_I(\boldsymbol{r}). \tag{3}$$

As in Ref. [9], we assume the following wave function to discuss the non-linear dynamics of the dipole plasmon resonance of this system.

$$|\Psi_{\alpha\beta}> = e^{i\alpha(t)Q}|\Psi_\beta> = e^{i\alpha(t)Q} e^{m\beta(t)[H,Q]}|\Psi_0> . \tag{4}$$

Here $|\Psi_0>$ is the ground state wave function. The operator Q is the dipole field given by

$$Q = \sum_{i=1}^{N} z_i. \tag{5}$$

The time evolution of the variables $\alpha(t)$ and $\beta(t)$ is determined according to the time-dependent variational principle,

$$\delta \int dt < \Psi_{\alpha\beta}|i\partial_t - H|\Psi_{\alpha\beta}> = 0. \tag{6}$$

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This leads to the following two coupled equations [9]

$$\dot{\beta} = \frac{\alpha}{m}, \tag{7}$$

$$\dot{\alpha}\partial_\beta < \Psi_\beta|Q|\Psi_\beta > \; + \partial_\beta < \Psi_\beta|H|\Psi_\beta > +\frac{\alpha^2}{2}\partial_\beta < \Psi_\beta|[Q,[H,Q]]|\Psi_\beta >= 0. \tag{8}$$

In order to find the phonon frequency, we requantise these equations of motion with a Hamiltonian formulation. One convenient choice of the canonical transformation is [9]

$$\beta \rightarrow q = \beta, \tag{9}$$

$$\alpha \rightarrow p = m\alpha < \Psi_\beta|[Q,[H,Q]]|\Psi_\beta >, \tag{10}$$

together with the Hamiltonian of

$$\mathcal{H} = \frac{p^2}{2M(\beta)} + U(\beta), \tag{11}$$

where the inertia and the potential are given by

$$M(\beta) = m^2 < \Psi_\beta|[Q,[H,Q]]|\Psi_\beta >, \tag{12}$$

$$U(\beta) = \; < \Psi_\beta|H|\Psi_\beta >, \tag{13}$$

respectively. For the dipole field (5), the inertia is easily evaluated to be $M(\beta) = mN$. After dropping the constant term, the collective potential is calculated as

$$U(\beta) = \int dxdydz V_I(x,y,z-\beta)\rho_0(x,y,z) = \int dxdydz V_I(x,y,z)\rho_0(x,y,z+\beta), \tag{14}$$

ρ_0 being the ground state density. To derive Eq. (14), we have used the transformation

$$e^{-m\beta[H,Q]}(x_i,y_i,z_i)e^{m\beta[H,Q]} = (x_i,y_i,z_i-\beta) \tag{15}$$

for the dipole field, and the fact that both the kinetic energy and the Coulomb interaction among the electrons in the Hamiltonian (1) are translational invariant [11]. Since we are interested in the leading order correction to the harmonic limit, we expand the ground state density in Eq. (14) in terms of β. Accordingly, we express the collective potential as

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$$U(\beta) = U_0 + \frac{k}{2}\beta^2 + \frac{k_4}{4}\beta^4 + \cdots. \tag{16}$$

The linear term in the expansion vanishes because of the stability of the ground state, and the third order term drops if the spherical symmetry is assumed for the ground state density. Using the Poisson equation (3), the coefficients k and k_4 are evaluated as

$$k = \frac{16\pi^2}{3}e^2 \int_0^\infty r^2 dr \rho_I(r)\rho_0(r), \tag{17}$$

$$k_4 = -\frac{16\pi^2}{54}e^2 \int_0^\infty r^2 dr \frac{d\rho_I(r)}{dr}\frac{d\rho_0(r)}{dr}, \tag{18}$$

respectively. Here we have assumed that the ionic density ρ_I has the spherical symmetry. The expression for k, Eq. (17), was first derived by Brack in the context of the sum rule approach [11,12].

Equations (17) and (18) are general expressions and valid for any form of the ionic and the electronic density distributions, as long as they are spherical. In order to get a more transparent formula, we further simplify them by using the jellium approximation. Here the ionic charge density is uniform in a sphere of radius $R = r_s N^{1/3}$, where r_s is the Wigner-Seitz radius. We thus assume

$$\rho_I(r) = \frac{3}{4\pi r_s^3}\theta(R - r), \tag{19}$$

where θ is the theta function. Substituting Eq. (19) to Eqs. (17) and (18), we obtain

$$k = \frac{Ne^2}{r_s^3}, \tag{20}$$

$$k_4 = \frac{4\pi}{18}\frac{e^2}{r_s}N^{2/3}\frac{d\rho_0(r)}{dr}\bigg|_{r=R}. \tag{21}$$

Here we have neglected the effect of spillout of the electron density outside the ionic background, which is order of $1/N$. To get an analytic expression for k_4, we approximate the electronic density by the error function as [13]

$$\rho_0(r) = \frac{3}{4\pi r_s^3}\text{erfc}\left(\frac{R - r}{a}\right), \tag{22}$$

where a is the surface diffuseness parameter for the electronic density. Substituting this density to Eq. (21), we finally obtain

$$k_4 = -\frac{e^2 N^{2/3}}{3a\sqrt{\pi}r_s^4}. \tag{23}$$

We now requantise the collective Hamiltonian $\mathcal{H}$ and obtain the phonon frequency. The frequency in the harmonic limit is given by

$$\omega_0 = \sqrt{\frac{k}{M}} = \sqrt{\frac{e^2}{mr_s^3}}, \tag{24}$$

which coincides with the Mie frequency. The leading correction to the harmonic limit is given by [9,10]

$$E_n = n\omega_0 - \frac{3k_4}{8k^2}n^2\omega_0^2 = n\omega_0 - \frac{1}{8\sqrt{\pi}}\frac{r_s^2}{ae^2}N^{-4/3}n^2\omega_0^2. \tag{25}$$

Taking the second derivative, the energy shift of the double phonon state is found to be

$$\Delta^{(2)}E = E_2 - 2E_1 - E_0 = -\frac{\omega_0^2}{4\sqrt{\pi}}\frac{r_s^2}{ae^2}N^{-4/3}. \tag{26}$$

Note that the dependence of $\Delta^{(2)}E/\omega_0$ on N is the same as that for the nuclear giant resonances [9]. Expressing it as a dependence of the volume of the system $N \sim L^3$, it is also the same as that for the photon spectrum in a small cavity [10]. All of them scale as $N^{-4/3} \sim L^{-4}$.

Let us now estimate numerically the shift of the frequency for Na clusters. Using the Wigner-Seits radius of $r_s = 4$ a.u., the Mie frequency (24) is evaluated as $\omega_0 = 3.39$ eV. Bertsch and Eckardt fitted the electronic density obtained by a self-consistent local density approximation by Eq. (22) and obtained $a = 2.14$ a.u. for $N = 198$ [13]. Assuming that the surface diffuseness a has a very weak dependense of N, the energy shift of the double phonon state (26) is estimated as

$$\Delta^{(2)}E = -0.45 \times N^{-4/3} \quad (eV), \tag{27}$$

which is extremely small compared with the phonon frequency ω_0 in the harmonic limit. For example, it is as small as -1.1×10^{-3} eV for $N=92$. This result is consistent with the recent experimental observation [7] that multiple dipole resonances are easily accessible for Na clusters.

In summary, we applied the time-dependent variational principle to the dipole plasmon resonance of alkali metal clusters to discuss its anharmonic properties. The uniform jellium approximation for the ionic density as well as the error function approximation for the electronic density lead to a simple analytic expression for the energy shift of the double phonon state. We found that the ratio of this quantity to the frequency in the harmonic limit scales as $N^{-4/3}$, which coincides with that for both nuclear giant resonances and for the photon spectrum in a small cavity. For Na clusters, we found that the anharmonic effects are almost negligible, which is consistent with both the previous TDLDA calculation and the recent experimental suggestion.

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